

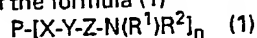
# (12) UK Patent Application (19) GB (11) 2 275 477 (13) A

(43) Date of A Publication 31.08.1994

|   |   |
|---|---|
| <p>(21) Application No 9403610.0</p> <p>(22) Date of Filing 25.02.1994</p> <p>(30) Priority Data<br/>(31) 05038445 (32) 26.02.1993 (33) JP</p>  | <p>(51) INT CL<sup>5</sup><br/>C09D 7/02 11/10 // C09D 133/00</p> <p>(52) UK CL (Edition M )<br/>C3V VABP VAD<br/>C3M MXAW M116C M145 M153<br/>C3W W225 W328C<br/>U1S S1390 S1391</p> |
| <p>(71) Applicant(s)<br/>Toyo Ink Manufacturing Co. Ltd<br/><br/>(Incorporated in Japan)<br/><br/>3-13, Kyobashi 2-chome, Chuo-ku, Tokyo 104, Japan</p> <p>(72) Inventor(s)<br/>Atsushi Endo<br/>Akimitsu Mochizuki<br/>Michichika Hikosaka<br/>Tsutomu Fujigamori</p> <p>(74) Agent and/or Address for Service<br/>J A Kemp &amp; Co<br/>14 South Square, Gray's Inn, LONDON, WC1R 5LX,<br/>United Kingdom</p> | <p>(56) Documents Cited<br/>US 4317682 A</p> <p>(58) Field of Search<br/>UK CL (Edition M ) C3M MXAW , C3V VABP VABR<br/>VABS VABT VAD<br/>INT CL<sup>5</sup> C09D</p>                |

(54) A water-based pigment dispersion

(57) A water-based dispersion capable of providing an excellent gloss when used to coat an article and exhibiting tinting strength, fluidity and storage stability, comprises 100 parts by weight of a pigment, 5 to 500 parts by weight, as a solid content, of a water-based resin and 0.1 to 30 parts by weight of a pigment dispersing agent of the formula (1)



wherein

P is an organic dyestuff residue or a heterocyclic ring residue,  
X is a divalent binding group consisting of 2 to 15 atoms selected from S, C, N, O and H atoms,  
Y is a direct bond, -N(R)- in which R is H, C<sub>1</sub>-C<sub>18</sub> alkyl or Q-N(R<sup>3</sup>)R<sup>4</sup> in which Q is C<sub>1</sub>-C<sub>6</sub> alkylene and each of R<sup>3</sup> and R<sup>4</sup> is independently an optionally substituted C<sub>1</sub>-C<sub>18</sub> alkyl group or R<sup>3</sup> and R<sup>4</sup> are together forming an optionally substituted heterocyclic ring which may contain N, O or S, or -O-,  
Z is C<sub>1</sub>-C<sub>6</sub> alkylene, and each of R<sup>1</sup> and R<sup>2</sup> is independently an optionally substituted C<sub>1</sub>-C<sub>18</sub> alkyl group or R<sup>1</sup> and R<sup>2</sup> are together forming an optionally substituted heterocyclic ring which may contain N, O or S, and n is of 1 to 3.

GB 2 275 477 A

## WATER-BASED PIGMENT DISPERSION

## Field of the Invention

The present invention relates to an organic solvent-free and water-based pigment dispersion which is excellent in the gloss of a coating and tinting strength and also excellent in fluidity and storage stability when used as a water-based coating composition or ink.

## Prior Art of the Invention

In recent years, coating compositions and inks are being converted to organic solvent-free and water-based ones due to increasing demands for the protection of resources, the protection of environments and improvement in working safety.

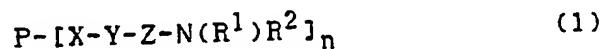
The properties which an organic solvent-free and water-based coating composition and ink are required to have are fluidity, storage stability, gloss of a coating, clearness and tinting strength, and this was also true of an organic solvent-containing coating composition and ink. Since, however, most of pigments have extremely poor suitability to water-based vehicles such as dispersibility, it is very difficult to obtain a coating composition or ink having satisfactory properties by a general dispersing method. The use of a variety of additives such as resins and surfactants for dispersing pigments in water-based vehicles has been hence studied. However, no organic solvent-free, water-based coating compositions and inks which have been obtained so far satisfy all of the above properties or exhibit no less adequate properties than existing organic solvent-containing coating compositions and inks. That is, some resins for dispersing pigments serve to give water-based pigment dispersions which are improved in

gloss of a coating, clearness and tinting strength to some extent, while the following critical problems remain to solve; the fluidity is impaired, the dispersion shows an increase in viscosity, or undergoes gelation, with time or there is an adverse effect on physical properties of a coating.

#### Summary of the Invention

It is an object of the present invention to provide a water-based pigment dispersion excellent in gloss of a coating, tinting strength, fluidity and storage stability.

The above object and advantages of the present invention are achieved by a water-based pigment dispersion comprising 100 parts by weight of a pigment, 5 to 500 parts by weight, as a solid content, of a water-based resin and 0.1 to 30 parts by weight of a pigment dispersing agent of the formula (1),



wherein:

P is an organic dyestuff residue or a heterocyclic ring residue,

X is a divalent binding group consisting of 2 to 15 atoms selected from S, C, N, O and H atoms,

Y is a direct bond,  $-N(R)-$  in which R is H, an alkyl group having 1 to 18 carbon atoms or  $Q-N(R^3)R^4$  in which Q is an alkylene group having 1 to 6 carbon atoms and each of  $R^3$  and  $R^4$  is independently an optionally substituted alkyl group having 1 to 18 carbon atoms or  $R^3$  and  $R^4$  are together forming an optionally substituted heterocyclic ring which may contain N, O or S, or  $-O-$ ,

Z is an alkylene group having 1 to 6 carbon atoms, and each of  $R^1$  and  $R^2$  is independently an optionally

substituted alkyl group having 1 to 18 carbon atoms or  $R^1$  and  $R^2$  are together forming an optionally substituted heterocyclic ring which may contain N, O or S, and  $n$  is an integer of 1 to 3.

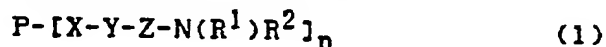
#### Detailed Description of the Invention

The present inventor has found that the above problems can be effectively overcome by incorporating 0.1 to 30 % by weight, per 100 parts by weight of a pigment, of the pigment dispersing agent of the above formula (1).

The water-based pigment dispersion of the present invention comprises a pigment, a water-based resin and the pigment dispersing agent of the formula (1).

The pigment used in the present invention includes a phthalocyanine pigment, an insoluble azo pigment, an azo lake pigment, an anthraquinone pigment, a quinacridone pigment, a dioxazine pigment, a diketopyrrolopyrrole pigment, an anthrapyridine pigment, an anthanthrone pigment, an indanthrone pigment, a flavanthrone pigment, a perinone pigment, a perylene pigment, a thioindigo pigment, carbon black, iron oxide, white lead, red lead, ultramarine, prussian blue, cobalt oxide, titanium dioxide, titanium oxide-coated mica, strontium chromate, titanium yellow, titanium black, zinc chromate, black iron oxide, molybdenum red, molybdenum white, lithopone, emerald green, cadmium yellow, cadmium red and cobalt blue.

The pigment dispersing agent used in the present invention has the formula (1),



wherein:

P is an organic dyestuff residue or a heterocyclic ring residue,

X is a divalent binding group consisting of 2 to

15 atoms selected from S, C, N, O and H atoms,

Y is a direct bond,  $-N(R)-$  in which R is H, an alkyl group having 1 to 18 carbon atoms or  $Q-N(R^3)R^4$  in which Q is an alkylene group having 1 to 6 carbon atoms and each of  $R^3$  and  $R^4$  is independently an optionally substituted alkyl group having 1 to 18 carbon atoms or  $R^3$  and  $R^4$  are together forming an optionally substituted heterocyclic ring which may contain N, O or S, or  $-O-$ ,

Z is an alkylene group having 1 to 6 carbon atoms, and each of  $R^1$  and  $R^2$  is independently an optionally substituted alkyl group having 1 to 18 carbon atoms or  $R^1$  and  $R^2$  are together forming an optionally substituted heterocyclic ring which may contain N, O or S, and

n is an integer of 1 to 3.

In the above formula (1), the organic dyestuff residue includes a phthalocyanine dyestuff residue, an insoluble azo dyestuff residue, an azo lake dyestuff residue, an anthraquinone dyestuff residue, a quinacridone dyestuff residue, a dioxazine dyestuff residue, a diketopyrrolopyrrole dyestuff residue, an anthrapyridine dyestuff residue, an anthanthrone dyestuff residue, an indanthrone dyestuff residue, a flavanthrone dyestuff residue, a perinone dyestuff residue, a perylene dyestuff residue, a thioindigo dyestuff residue. Any one of the above dyestuff residues may be used, while it is industrially advantageous to use an organic dyestuff residue having a hue similar to that of the pigment used.

The heterocyclic ring includes thiophene, furan, xanthene, pyrrole, imidazole, isoindoline, isoindolinone, benzimidazolone, indole, quinoline, carbazole, acridine, acridone and anthraquinone.

When P is a heterocyclic ring residue, a colorless or almost colorless pigment dispersing agent can be

obtained, which is preferred for use as a general pigment dispersing agent.

X is a binding group consisting of 2 to 15 atoms selected from S, C, N, O and H atoms, such as  $-\text{SO}_2-$ ,  $-\text{CO}-$ ,  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{-NHCOCH}_2-$ ,  $-\text{O}-$ ,  $-\text{COO}-$ ,  $-\text{NH}-$  or a combination thereof, preferably  $-\text{SO}_2-$ ,  $-\text{CO}-$ ,  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{-NHCOCH}_2-$ .

In the above formula (1), each of  $\text{R}^1$  and  $\text{R}^2$  is independently an optionally substituted alkyl group having 1 to 18 carbon atoms or  $\text{R}^1$  and  $\text{R}^2$  are together forming an optionally substituted heterocyclic ring which may contain N, O or S. The above alkyl group is preferably a lower alkyl group including methyl, ethyl, propyl and butyl. The alkyl group may be branched or substituted so long as the total of carbon atoms is 18 or less. Further,  $\text{R}^1$  and  $\text{R}^2$  may together form a 5- or 6-membered heterocyclic ring containing N, O or S.

In the above formula (1), Y is a direct bond,  $-\text{N}(\text{R})-$  in which R is H, an alkyl group having 1 to 18 carbon atoms or  $\text{Q-N}(\text{R}^3)\text{R}^4$  in which Q is an alkylene group having 1 to 6 carbon atoms and each of  $\text{R}^3$  and  $\text{R}^4$  is independently an optionally substituted alkyl group having 1 to 18 carbon atoms or  $\text{R}^3$  and  $\text{R}^4$  are together forming an optionally substituted heterocyclic ring which may contain N, O or S, or  $-\text{O}-$ . The above alkyl group for each of  $\text{R}^3$  and  $\text{R}^4$  is preferably a lower alkyl group including methyl, ethyl, propyl and butyl. The alkyl group may be branched or substituted so long as the total of carbon atoms is 18 or less. Further,  $\text{R}^3$  and  $\text{R}^4$  may together form a 5- or 6-membered heterocyclic ring containing N, O or S.

The pigment dispersing agent used in the present invention can be produced by a method in which a substituent such as  $-\text{SO}_2\text{Cl}-$ ,  $-\text{COCl}-$ ,  $\text{CH}_2\text{Cl}-$  or  $\text{CH}_2\text{NHCOCH}_2\text{Cl}-$  is first introduced into the organic dyestuff or heterocyclic ring by

a known method, and then allowed to react with a compound having the structure of  $Y-Z-N(R^1)R^2$  described in the formula (1). The compound corresponding to Y and  $Z-N(R^1)R^2$  N,N-dimethylaminomethyl, N,N-dimethylaminoethyl, N,N-dimethylaminopropyl, N,N-dimethylaminoamyl, N,N-dimethylaminobutyl, N,N-diethylaminoethyl, N,N-diethylaminoethoxypropyl, N,N-diethylaminobutyl, N,N-diethylaminopentyl, N,N-dipropylaminobutyl, N,N-dibutylaminopropyl, N,N-dibutylaminoethyl, N,N-dibutylaminobutyl, N,N-diisobutylaminopentyl, N,N-methyl-laurylaminoethyl, N,N-ethyl-hexylaminoethyl, N,N-distearylaminoethyl, N,N-dioleylaminoethyl, N,N-distearylaminobutyl, N-aminoethylpiperidine, N-aminoethyl-4-pipecoline, N-aminoethylmorpholine, N-aminopropylpiperidine, N-aminopropyl-2-pipecoline, N-aminopropyl-4-pipecoline, N-aminopropylmorpholine, N-aminomethylpiperidine, N-hydroxymethylpiperidine, N-hydroxymethylpiperidine, N-hydroxypropylpiperidine, N-hydroxyethylpipecoline, N-hydroxypropylpipecoline, N-hydroxymethylpyrrolidine, N-hydroxyethylmorpholine, N-hydroxybutylmorpholine, N-aminopropylmorpholine, N-aminopropylthiazolidine, and N,N,N',N'-tetramethyl diethylene triamine, etc.

The above pigment dispersing agent may be used in a dry powder state when the pigment is dispersed, or it may be mixed with the pigment before use. Further, the above pigment dispersing agent may be used as a solution or dispersion thereof in a solvent or a mineral acid. In this case, the pigment dispersing agent is added to a slurry of the pigment in water or a solvent to be adsorbed on the pigment surface. When the pigment is an azo pigment, the pigment dispersing agent in a powder, solution or dispersion state may be added during the coupling reaction whereby the pigment dispersing agent is adsorbed on the pigment surface.

Then, the mixture is filtered and then dried as required. When the pigment is a phthalocyanine pigment, a quinacridone pigment or a dioxazine pigment, the pigment dispersing agent in a powder, solution or dispersion state may be added during the pigment forming step such in a salt milling method or sulfuric acid dissolving method, whereby the pigment dispersing agent is adsorbed on the pigment. Then, the mixture is filtered and then dried as required.

The amount of the pigment dispersing agent per 100 parts by weight is 0.1 to 30 parts by weight. When this amount is less than 0.1 part by weight, the object of the present invention is hardly accomplished. When it exceeds 30 parts by weight, no further effect is obtained.

The water-based resin used in the present invention includes water-dispersible resins or water-soluble resins such as an acrylic copolymer resin, a styrene-acrylate copolymer resin, a styrene-maleate copolymer resin, an alkyd resin, an epoxy resin, a polyester resin and a urethane resin. Particularly preferred is a water-dispersible or water-soluble acrylic copolymer resin.

The above acrylic copolymer resin is obtained by a method in which 50 to 80 % by weight of alkyl (meth)acrylate, 5 to 30 % by weight of a carboxyl group-containing monomer such as acrylic acid, methacrylic acid, maleic acid or itaconic acid and 0 to 20 % by weight of other monomer are emulsion polymerized or solution polymerized in an aqueous solvent. The above acrylic copolymer has a weight average molecular weight of 5,000 to 300,000 and an acid value of 1 to 200. The above alkyl (meth)acrylate includes methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, isopropyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-hexyl



(meth)acrylate and lauryl (meth)acrylate. The above "other monomer" includes 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, acrylamide, N-methylolacrylamide, diacetoneacrylamide, glycidyl (meth)acrylate, styrene, vinyltoluene, vinyl acetate, acrylonitrile, vinyl alcohol and ethylene.

The above water-dispersible resin can be produced by dropwise adding a mixture of the above monomers to an aqueous medium containing an emulsifier and emulsion-polymerizing these. The aqueous medium may contain a dispersing agent having a high molecular in place of, or together with, the emulsifier. In the above water-dispersible resin, the carboxylic acid integrated with a resin may be neutralized by adding an amine or ammonia for dispersing the water-dispersible resin in an aqueous dispersion. For example, the water-dispersible resins can be obtained by neutralizing an acrylic copolymer resin having a free carboxylic acid, obtained by the polymerization in a hydrophilic organic solvent, with an organic amine and then adding water.

The above water-soluble resin can be produced by neutralizing an acrylic copolymer resin having a free carboxylic acid, obtained by the polymerization of the above monomers, with an organic amine and then adding water.

The aqueous medium used for the production of the water-based resin used in the present invention may be water alone or a mixture of water with up to 50 % by weight of an alcohol such as ethyl alcohol, isopropyl alcohol, n-propyl alcohol or n-butanol or a water-miscible organic solvent such as mono- or dialkyl ether of ethylene glycol or diethylene glycol.

The amount of the water-based resin per 100 parts by weight of the pigment is 5 to 500 parts by weight,

preferably 5 to 200 parts by weight. When this amount is less than 5 parts by weight, it is difficult to disperse the pigment completely. When it is more than 500 parts by weight, the coloring strength is low, and the pigment dispersion is not suitable for use as a coating composition or a printing ink.

The water-based pigment dispersion of the present invention can be produced by a method in which the pigment and the pigment dispersing agent are incorporated into a dispersion or solution of the water-based resin. Further, it can be also produced by a method in which a pigment composition containing the pigment and the pigment dispersing agent is incorporated into a dispersion or solution of the water-based resin. The pigment and the pigment dispersing agent, or the pigment composition, can be dispersed in a solution or dispersion of the water-based resin with a dispersing apparatus such as a dissolver, a high-speed mixer, a homomixer, a sand mill or an attriter.

The water-based pigment dispersion of the present invention can be used as a water-based coating composition, a water-based ink or a concentrate of each of these.

#### Examples

The present invention will be detailed hereinafter with reference to Examples, in which "part" stands for "part by weight".

#### Preparation Example 1

306 Parts dimethylaminopropylamine was added to 1,000 parts of water, and a water-based wet cake containing 145 parts of copper phthalocyanine sulfonyl chloride (containing 1.5 chlorosulfonyl groups per mole on average) was added. The mixture was stirred at 65°C for 2 hours.

The reaction mixture was filtered and the remaining solid was washed with water and dried at 80°C to give 230 parts of a blue powder (Pigment dispersing agent A).

#### Preparation Example 2

474 Parts of dibutylaminomethylamine was added to 2,000 parts of dimethylformamide, and 135 parts of chloromethyl copper phthalocyanine (containing 2 chloromethyl groups per mole on average) was added. The mixture was stirred at 100°C for 3 hours. The reaction mixture was filtered and the remaining solid was washed with water and dried at 80°C to give 250 parts of a blue powder (Pigment dispersing agent B).

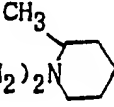
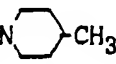

#### Preparation Example 3

260 Parts diethylaminopropylamine was added to 1,000 parts of water, and a water-based wet cake containing 136 parts of chloroacetoaminomethyl copper phthalocyanine (containing one chloroacetoaminomethyl group per mole on average) was added. The mixture was stirred at 60°C for 1 hour. The reaction mixture was filtered and the remaining solid was washed with water and dried at 80°C to give 230 parts of a blue powder (Pigment dispersing agent C).

#### Preparation Examples 4 - 19

Pigment dispersing agents D to S shown in Table 1 were prepared according to Preparation Examples 1 to 3.

Table 1

| PEX. | Pigment<br>dispersing<br>agent | Organic dyestuff<br>or heterocyclic<br>ring | Substituent   | Number of<br>substituent |
|------|--------------------------------|---|---|--------------------------|
| 1    | A                              | C.I. Pigment Blue 15                        | $-\text{SO}_2\text{NH}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$   | 1.5                      |
| 2    | B                              | C.I. Pigment Blue 15                        | $-\text{CH}_2\text{NHCH}_2\text{N}(\text{C}_4\text{H}_9)_2$   | 2                        |
| 3    | C                              | C.I. Pigment Blue 15                        | $-\text{CH}_2\text{NHCOCH}_2-$<br>$\text{NH}(\text{CH}_2)_3\text{N}(\text{C}_4\text{H}_9)_2$  | 1                        |
| 4    | D                              | C.I. Pigment Violet 19                      | $-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$   | 2                        |
| 5    | E                              | C.I. Pigment Violet 19                      | $-\text{CH}_2\text{NHCOCH}_2-$<br>$\text{NH}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2$  | 1                        |
| 6    | F                              | C.I. Pigment Violet 23                      | $-\text{SO}_2\text{NH}(\text{CH}_2)_3(\text{C}_3\text{H}_7)_2$  | 1                        |
| 7    | G                              | C.I. Pigment Orange 43                      | $-\text{CH}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{NHC}_{18}\text{H}_{37}$  | 1                        |
| 8    | H                              | C.I. Pigment Yellow 24                      | $-\text{SO}_2\text{NH}(\text{CH}_2)_2\text{N}$<br>   | 1                        |
| 9    | I                              | C.I. Pigment Red 178                        | $-\text{SO}_2\text{NH}(\text{CH}_2)_2\text{N}$<br> | 1                        |
| 10   | J                              | C.I. Pigment Yellow 108                     | $-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}$<br> | 1                        |
| 11   | K                              | C.I. Pigment Red 168                        | $-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{C}_3\text{H}_7)_2$  | 1                        |
| 12   | L                              | C.I. Pigment Blue 60                        | $-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$   | 2                        |
| 13   | M                              | C.I. Pigment Red 88                         | $-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$   | 1                        |
| 14   | N                              | C.I. Pigment Yellow 83                      | $-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2$  | 1                        |
| 15   | O                              | C.I. Pigment Red 2                          | $-\text{CONH}(\text{CH}_2)_3\text{N}(\text{C}_4\text{H}_9)_2$   | 1                        |
| 16   | P                              | C.I. Pigment Red 254                        | $-\text{SO}_2\text{NH}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$   | 1                        |
| 17   | Q                              | Anthraquinone                               | $-\text{CONH}(\text{CH}_2)_3\text{N}(\text{C}_3\text{H}_7)_2$   | 1                        |
| 18   | R                              | Acridone                                    | $-\text{SO}_2\text{NH}(\text{CH}_2)_2\text{N}(\text{C}_4\text{H}_9)_2$  | 1                        |
| 19   | S                              | Carbazole                                   | $-\text{SO}_2\text{NH}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$   | 1                        |

## Example 1

9.9 Parts of C.I. Pigment Blue 15:1, 0.1 part of  
Pigment dispersing agent A, 12.5 parts of an acrylic resin

solution (solid content 20 %) having an acid value of 60, 20 parts of ion-exchanged water and 150 parts of alumina beads having a diameter of 3 mm were placed in a 225 ml glass container, and dispersed with a paint conditioner for 3 hours. Then, 37.5 parts of the same acrylic resin solution as that described above and 4.3 parts of a methylated melamine resin (trade name: Cymel 303, supplied by Mitsui-Cyanamid) were added to and mixed with the above mixture to give a water-based coating composition. The so-obtained coating composition was coated on a PET film with a 4-mil film applicator and baked at 140°C for 30 minutes to give a coating having excellent gloss. The coating was measured for a 20° gloss with a digital angle-variable gloss meter to show 62°.

#### Examples 2 - 23

Coating compositions were prepared from a variety of pigments and the pigment dispersing agents B to S, and the so-obtained coating compositions were coated on PET films, in the same manner as in Example 1, whereby coatings having excellent gloss were obtained. The coatings were measured for a 20° gloss with a digital angle-variable gloss meter. Table 2 shows the results.

#### Comparative Examples

Coating compositions were prepared from the same pigments as those used in Examples 1 to 23 without using the pigment dispersing agents. And, the so-obtained coating compositions were coated on PET films in the same manner as in Example 1. The resultant coatings were poor in gloss as compared with those obtained from coating compositions containing the pigment dispersing agents. Table 2 shows the results.

Table 2

|       | Pigment                 | Pigment<br>dispersing<br>agent | Amount<br>ratio* | 20°<br>gloss |
|-------|-------------------------|--------------------------------|------------------|--------------|
| CEx   | C.I. Pigment Blue 15:1  | -                              | 10/0             | 48           |
| Ex.1  | C.I. Pigment Blue 15:1  | A                              | 9.9/0.1          | 62           |
| Ex.2  | C.I. Pigment Blue 15:1  | A                              | 9.5/0.5          | 66           |
| Ex.3  | C.I. Pigment Blue 15:1  | A                              | 9/1              | 69           |
| Ex.4  | C.I. Pigment Blue 15:1  | B                              | 9/1              | 69           |
| Ex.5  | C.I. Pigment Blue 15:1  | C                              | 9/1              | 68           |
| CEx   | C.I. Pigment Violet 19  | -                              | 10/0             | 56           |
| Ex.6  | C.I. Pigment Violet 19  | D                              | 9/1              | 78           |
| Ex.7  | C.I. Pigment Violet 19  | E                              | 9/1              | 75           |
| Ex.8  | C.I. Pigment Violet 19  | R                              | 9/1              | 70           |
| CEx.  | C.I. Pigment Violet 23  | -                              | 10/0             | 45           |
| Ex.9  | C.I. Pigment Violet 23  | F                              | 9.5/0.5          | 62           |
| Ex.10 | C.I. Pigment Violet 23  | S                              | 9.5/0.5          | 59           |
| CEx.  | C.I. Pigment Orange 43  | -                              | 10/0             | 51           |
| Ex.11 | C.I. Pigment Orange 43  | G                              | 9/1              | 65           |
| CEx.  | C.I. Pigment Yellow 24  | -                              | 10/0             | 35           |
| Ex.12 | C.I. Pigment Yellow 24  | H                              | 9/1              | 68           |
| CEx.  | C.I. Pigment Red 178    | -                              | 10/0             | 52           |
| Ex.13 | C.I. Pigment Red 178    | I                              | 9/1              | 66           |
| CEx.  | C.I. Pigment Yellow 108 | -                              | 10/0             | 45           |
| Ex.14 | C.I. Pigment Yellow 108 | J                              | 8/2              | 59           |
| CEx.  | C.I. Pigment Red 168    | -                              | 10/0             | 51           |
| Ex.15 | C.I. Pigment Red 168    | K                              | 9/1              | 79           |
| CEx.  | C.I. Pigment Blue 60    | -                              | 10/0             | 33           |
| Ex.16 | C.I. Pigment Blue 60    | L                              | 9/1              | 68           |
| CEx.  | C.I. Pigment Red 88     | -                              | 10/0             | 34           |
| Ex.17 | C.I. Pigment Red 88     | M                              | 9/1              | 58           |
| CEx.  | C.I. Pigment Red 23     | -                              | 10/0             | 57           |
| Ex.18 | C.I. Pigment Red 23     | N                              | 9/1              | 77           |
| CEx.  | C.I. Pigment Red 48:4   | -                              | 10/0             | 45           |
| Ex.19 | C.I. Pigment Red 48:4   | N                              | 9.5/0.5          | 76           |
| CEx.  | C.I. Pigment Yellow 83  | -                              | 10/0             | 61           |
| Ex.20 | C.I. Pigment Yellow 83  | P                              | 9.5/0.5          | 84           |
| CEx.  | C.I. Pigment Red 177    | -                              | 10/0             | 32           |
| Ex.21 | C.I. Pigment Red 177    | Q                              | 9/1              | 79           |
| CEx.  | C.I. Pigment Black 11   | -                              | 10/0             | 68           |
| Ex.22 | C.I. Pigment Black 11   | A                              | 9/1              | 81           |
| CEx.  | C.I. Pigment Red 101    | -                              | 10/0             | 78           |
| Ex.23 | C.I. Pigment Red 101    | C                              | 9/1              | 91           |

Ex. = Example, CEx. = Comparative Example  
Amount ratio = Pigment/Pigment dispersing agent

CLAIMS

1. A water-based pigment dispersion comprising 100 parts by weight of a pigment, 5 to 500 parts by weight, as a solid content, of a water-based resin and 0.1 to 30 parts by weight of a pigment dispersing agent of the formula (1),



10 wherein:

P is an organic dyestuff residue or a heterocyclic ring residue,

X is a divalent binding group consisting of 2 to 15 atoms selected from S, C, N, O and H atoms,

- 15 Y is a direct bond, -N(R)- in which R is H, an alkyl group having 1 to 18 carbon atoms or Q-N(R<sup>3</sup>)R<sup>4</sup> in which Q is an alkylene group having 1 to 6 carbon atoms and each of R<sup>3</sup> and R<sup>4</sup> is independently an optionally substituted alkyl group having 1 to 18 carbon atoms or R<sup>3</sup> and R<sup>4</sup> are together  
20 forming an optionally substituted heterocyclic ring which may contain N, O or S, or -O-,

Z is an alkylene group having 1 to 6 carbon atoms, and each of R<sup>1</sup> and R<sup>2</sup> is independently an optionally substituted alkyl group having 1 to 18 carbon atoms or R<sup>1</sup>  
25 and R<sup>2</sup> are together forming an optionally substituted heterocyclic ring which may contain N, O or S, and

n is an integer of 1 to 3.

2. A water-based pigment dispersion according to claim 1, wherein X is a divalent binding group selected from  $\text{-SO}_2\text{-}$ ,  $\text{-CO-}$ ,  $\text{-CH}_2\text{-}$  and  $\text{-CH}_2\text{NHCOCH}_2\text{-}$ .
- 5 3. A water-based pigment dispersion according to claim 1 or 2, wherein the water-based resin is an acrylic copolymer resin.
4. A water-based pigment dispersion according to  
10 any one of the preceding claims, wherein the water-based resin is present in an amount of 5 to 200 parts by weight as a solid content.
5. An article coated with a water-based pigment  
15 dispersion according to any one of the preceding claims.
6. A coating composition substantially as hereinbefore described in any one of Examples 1 to 23.



**Patents Act 1977**  
**Examiner's report to the Comptroller under Section 17**  
**(True Search report)**

Application number  
GB 9403610.0

- 16 -

**Relevant Technical Fields**

(i) UK Cl (Ed.M) C3V (VABP, VABR, VABS, VABT, VAD)  
C3M (MXAW)

(ii) Int Cl (Ed.5) C09D

Search Examiner  
K MACDONALD

Date of completion of Search  
19 MAY 1994

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii)

Documents considered relevant following a search in respect of Claims :-  
1-6

**Categories of documents**

- |  |   |
|--|---|
| <p><b>X:</b> Document indicating lack of novelty or of inventive step.</p> <p><b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p><b>A:</b> Document indicating technological background and/or state of the art.</p> | <p><b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.</p> <p><b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p><b>&amp;:</b> Member of the same patent family; corresponding document.</p> |
|--|---|

| Category | Identity of document and relevant passages                                  | Relevant to claim(s) |
|----------|---|----------------------|
| X        | US 4317682 (TOYO INK) Claim 1; column 3, lines 61-62; column 4, lines 21-23 | at least Claim 1     |

**Databases:** The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).